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(54) Title: SECURITY TONER AND PROCESS FOR USING SAME

(57) Abstract

A liquid developer for use in electrostatic imaging processes in order to obtain an image of a more permanent nature than has usually been obtained hitherto, comprises (a) an insulating non-polar carrier liquid; and (b) pigmented polymer toner particles micro-dispersed in the carrier liquid, the toner particles comprising at least one sublimable dye. The sublimable dye may be substantially insoluble in the carrier liquid or it may be soluble therein, at least at elevated (fusing) temperatures, depending on whether a background effect is desired in the final image.

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SECURITY TONER AND PROCESS FOR USING SAME

FIELD OF THE INVENTION

The present invention relates to the field of electrophotography, and more particularly to improved liquid developers for use therein, as well as to an electrostatic imaging process using said liquid developers.

BACKGROUND OF THE INVENTION

In electrophotography, the particles which contain the coloring material are generally attached to the final substrate, e.g. paper, by fairly weak forces. This is especially true of most powder toners. Even in the case of liquid toners, however, vigorous erasing with a pencil eraser will remove the toner, often without leaving a trace. On the other hand, there may be circumstances in which a more permanent image is desirable. For example, many countries have a requirement that archival material be printed in a manner which leaves an image even after erasure as just described. The present invention addresses and solves the problem of creating a more permanent final image in electrophotography, than has generally been obtained hitherto.

It is accordingly an object of the present invention to provide a substrate which includes a final image of a permanent nature resulting from an electrophotographic process.

It is another object of the present invention to provide a liquid developer, for use in electrostatic imaging processes, adapted to impart to a substrate a final image of a permanent nature. Yet other objects of the invention will be apparent from the description which follows.

SUMMARY OF THE INVENTION

In accordance with one aspect of the invention, there is provided a liquid developer for use in electrostatic imaging processes, such developer comprising: (a) an insulating non-polar carrier liquid; and (b) pigmented polymer toner particles micro-dispersed in the carrier liquid, the toner particles comprising at least one sublimable dye. In the present specification and claims,

the term "sublimable dye" is intended to mean a dye which has the property of sublimation, when heated at above ambient temperatures.

The sublimable dye may be in one embodiment substantially insoluble in the carrier liquid. In another embodiment, the sublimable dye may be sufficiently soluble in the carrier liquid such that the background of the final image will have a slight though uniform coloration. In yet another embodiment, the sublimable dye may be substantially insoluble in the carrier liquid at ambient temperatures, but is sufficiently soluble at elevated temperatures e.g. at the temperature of fusing, so that the background of the final image will have a slight though uniform coloration. If the dye is soluble in the carrier liquid at fusing temperatures it is not necessary that the dye be sublimable.

While a liquid developer is preferred, the invention is also applicable to powder toners comprising a polymer, a pigment and a sublimable dye.

In accordance with another aspect of the invention, there is provided an electrostatic imaging process, comprising the steps of: forming a latent electrostatic image on a photoconductive surface; applying to such surface charged toner particles from a liquid developer according to the invention, thereby forming a toner image on said surface; and transferring the resultant toner image to a substrate.

DETAILED DESCRIPTION OF THE INVENTION

In one embodiment of the invention the liquid developer comprises a carrier liquid and pigmented polymer toner particles as in known liquid developers. However, the toner material of the present invention includes a sublimable dye. When this dye has a very low solubility in the carrier liquid, then during the process of fusing the toner and fixing it to the paper by heat, the dye is evaporated onto, and into, the paper, thus coloring the fibers of the paper. When the toner particles are removed, the underlying substrate is seen to be colored. This color has penetrated deeply into the paper and cannot be removed except by

destroying the paper. When the dye is slightly soluble in the carrier liquid, then the background will be slightly and uniformly colored, which has the added advantage of making counterfeiting even more difficult. If a squeegee roller is used to remove most of the carrier liquid, then the background coloring is lower. In another embodiment of the invention, the dye is not soluble in the carrier liquid at room temperatures, but is somewhat soluble at higher (e.g. at fusing) temperatures. In the fusing step, the dye dissolves in the residual carrier liquid and is drawn into the paper with the liquid, thus staining the underlying paper substrate.

While the specific embodiments tested include the toner particles as part of a liquid developer, the invention is also applicable to powder toners comprising a polymer, a pigment and a sublimable dye.

Further while for the specific embodiments tested the dye is a sublimable dye, the principles of the invention are believed applicable for a dye which does not sublime at the fusing temperature, but which has low (or substantially no) solubility in the carrier liquid at room temperature and has substantial solubility in the carrier liquid at fusing temperatures.

SPECIFIC EMBODIMENTS

Liquid developers in accordance with the present invention were prepared using as toner polymer Surlyn 1855 (now known as Surlyn 9020) and a variety of dyes. The pigment is dispersed in the polymer and the material is cooled, shredded and ground all in the presence of carrier liquid. Comparison experiments using high concentrations (e.g. 20 or 25%) of conventional black pigment such as Mogul L did not create a permanent image in the final substrate; this result was not altered when Alkali Blue at 10% of the Mogul L was added, in order to overcome the slightly brown hue of the Mogul L.

According to a particular embodiment of the present invention, the sublimable dye is added during the cool grinding step. Other polymers useful in the practice of the

present invention, in addition to Surlyn 1855/9020, are other Surlyns, Elvax II polymers and Elvax I polymers, as well as other suitable polymers known in the field and mixtures of polymers. The addition of the sublimable dye is presently believed to not substantially affect the imaging process, except for the fact that it creates a more permanent final image in the substrate.

In the experiments, the carrier liquid (see also the description below) was Peneteck (Penreco, a Penzoil division), however, the use of Isopar (a trademark of the Exxon Corporation), e.g., Isopar L, or other carrier liquid would only affect the results to the extent that the solubility of the dye may vary according to the carrier liquid selected.

Persons skilled in the art will be aware that in liquid-developed electrostatic imaging, in general terms, the toner particles are dispersed in an insulating non-polar liquid carrier, generally an aliphatic hydrocarbon fraction; such fraction may have a high-volume resistivity above 10^9 ohm cm, a dielectric constant below 3.0 and a low vapor pressure (less then 10 torr. at 25°C). The liquid developer system preferably further comprises so-called charge directors, i.e. compounds capable of imparting to the toner particles an electrical charge of the desired polarity and uniform magnitude so that the particles may be electrophoretically deposited on the photoconductive surface to form a toner image.

In the course of the process, liquid developer is applied to the photoconductive imaging surface, regions of which are at a first, image, potential and regions of which are at a, second, background potential together forming a latent image. The charged toner particles in the liquid developer film migrate to the image regions forming the developed image.

Charge director molecules play an important role in the above-described developing process in view of their function of controlling the polarity and magnitude of the charge on the toner particles. The choice of a particular charge

director for use in a specific liquid developer system, will depend on a comparatively large number of physical characteristics of the charge director compound, inter alia its solubility in the carrier liquid, its chargeability, its high electric field tolerance, its release properties, its time stability, etc. All these characteristics are crucial to achieve high quality imaging, particularly when a large number of impressions are to be produced.

A wide range of charge director compounds for use in liquid-developed electrostatic imaging are known from the prior art. Pertinent examples of charge director compounds are ionic compounds, particularly metal salts of fatty acids, metal salts of sulfosuccinates, metal salts of oxyphosphates, metal salts of alkylbenzene-sulphonic acid, metal salts of aromatic carboxylic acids or sulfonic acids, as well as zwitterionic and non-ionic compounds, such as polyoxyetheylated alkylamines, polyvinylpyrrolidone, lecithin, organic acid esters of polyvalent alcohols, etc.

As stated above, the insulating non-polar liquid carrier, which should preferably also serve as the solvent for the charge director compounds utilized according to the invention, is most suitably an aliphatic hydrocarbon fraction having suitable electrical and other physical properties. Preferred solvents are the series of branched-chain aliphatic hydrocarbons and mixtures thereof, e.g. the isoparaffinic hydrocarbon fractions having a boiling range above about 155°C.

In the exemplified embodiments described herein, the printing process is carried out on a Savin 870 copier using a "hot plate" heater. The temperature of the hot plate is about 240°C and the image is estimated to reach about 110°C.

Examples of sublimable dyes are the following:

(A) Sublimable dyes having a high solubility at elevated temperatures: NEPTUN BLUE 627 LD (BASF), BLUE ANILINE WATER SOLUBLE (Kalaf);

(B) Sublimable dyes apparently soluble in carrier liquid:TERASIL ROT G (Ciba Geigy), WAXOLINE BLUE A (ICI),RESOLINE ROT FB 200% (Bayer), RHODAMINE FB (Bayer);

and

(C) Sublimable dyes apparently substantially insoluble in carrier liquid: RESOLINE BLAU FBL (Bayer), PERSIAN BLUE P5R (ICI), PROCION TURQUOISE H-A (ICI), RHODAMINE B (BASF).

Without detracting from the generality of the invention, the following Examples illustrate the use of particular sublimable dyes in accordance with the present invention. The given % indicates % of the dye in total non-volatile solids (NVS) in the developer.

EXAMPLE 1: Production of liquid developer.

Part (a): Dispersion

10 parts by weight of Surlyn 9020 (E. I. du Pont) and 5 parts by weight of Peneteck are mixed at low speed in a jacketed double planetary mixer connected to an oil heating unit, for 1.5 hours, the heating unit being set at 160°C. The mixture is estimated to be at about 130°C. 15 parts by weight Peneteck pre-heated to 120°C are added to the mixer and mixing is continued at high speed for one hour. The heating unit was then disconnected and the warm material is discharged into aluminum pans. When the mixture cools it is first passed through a meat grinder and then through a small stone mill such as a coffee grinder to reduce the particle size in preparation for the grinding step.

Part (b): Grinding

100 g. of the product of part (a) is mixed with 120 g. of Peneteck, approximately 8.25 g. of Mogul L (Cabot) carbon black and sublimable dye in the amount calculated to give the % dye in total non-volatile solids indicated below. Optionally, small amounts of Alkali Blue pigment and aluminum stearate are also added. The mixture is milled for 19 hours in an attritor cooled to 30°C, to obtain a concentrated dispersion of toner particles.

Part (c): Preparation and addition of charge director

A four-necked, 2 liter glass reactor fitted with a mechanical stirrer and a reflux condenser, is charged with 30 g. of lecithin, 30 g. of basic barium petronate and 513 g. of Isopar H. The materials are mixed until the solids are dissolved. Six grams of 1-vinyl-2-pyrrolidone are added

and the mixture is heated to 70°C while stirring is continued. Six grams of lauroyl peroxide dissolved in 15 g. of Isopar H (by sonication) is added to the mixture. The temperature is raised to 95°C and the reaction is allowed to proceed under stirring for 24 hours, in a nitrogen atmosphere. The mixture is then centrifuged at 9,000 rpm for 1/2 hour to yield the charge director composition. The charge director composition is added to the dispersion obtained in part (b), above, in a proportion of about 3% by weight of solids to the solids in the dispersion. Additional Peneteck is added to reduce the proportion of non-volatile solids to 1.5%.

EXAMPLE 2

A liquid developer is prepared as in Example 1, using 15% NVS NEPTUN BLUE 627 LD (BASF) and is utilized in printing as recited above. After removal of the pigmented polymer material a vivid blue image was left on printer's stock (which the carrier liquid in the developer easily wets) but poor transfer to Savin 2000+ paper, with a pale blue background image. No image was seen on the reverse side of the paper.

EXAMPLE 3

A liquid developer was prepared as in Example 1, using 10% or 15% NVS BLUE ANILINE WATER SOLUBLE (Kalaf) and was utilized in printing as recited above. After removal of the pigmented polymer material a blue image was left on both Savin 2000+ and printer's stock paper. The paper had a very slight blue tinge in the background regions. A very pale blue image was also seen on the reverse side of the paper.

EXAMPLE 4

A liquid developer was prepared as in Example 1, using 10% NVS TERASIL ROT G (Ciba Geigy) and was utilized in printing as recited above. After removal of the pigmented polymer material, a strong red image is left on printer's stock and a pale image on Savin 2000+ paper. A red image is also seen on the reverse side of the paper and the background regions have a slight red tinge.

EXAMPLE 5

A liquid developer is prepared as in Example 1, using 10% NVS WAXOLINE BLUE A (ICI) and is utilized in printing as recited above. After removal of the pigmented polymer material, a pale blue image is left on printer's stock and on Savin 2000+ paper. A very pale blue image is also seen on the reverse side of the paper and the background regions have a slight blue tinge.

EXAMPLE 6

A liquid developer is prepared as in Example 1, using 10% NVS RESOLINE ROT FB 200% (Bayer) and is utilized in printing as recited above. After removal of the pigmented polymer material, a pale red image is left on printer's stock and on Savin 2000+ paper. A paler red image is also seen on the reverse side of the paper and the background regions have a slight red tinge.

EXAMPLE 7

A liquid developer is prepared as in Example 1, using 10% NVS RHODAMINE FB (Bayer) and is utilized in printing as recited above. After removal of the pigmented polymer material, a strong red image is left on printer's stock and on Savin 2000+ paper. A slight red image is also seen on the reverse side of the Savin 2000+ paper. The background regions have a slight red tinge, showing some dye solubility at room temperature.

EXAMPLE 8

A liquid developer is prepared as in Example 1, using 10% NVS RESOLINE BLAU FBL (Bayer) and is utilized in printing as recited above. After removal of the pigmented polymer material, a pale blue image is left on printer's stock and on Savin 2000+ paper. There is no background coloring and no image is seen on the reverse side of the paper.

EXAMPLE 9

A liquid developer is prepared as in Example 1, using 10% NVS PERSIAN BLUE P5R (ICI) and is utilized in printing as recited above. After removal of the pigmented polymer material, a pale black image is left on printer's stock and

on Savin 2000+ paper. There is no background coloring and no image is seen on the reverse side of the paper.

EXAMPLE 10

A liquid developer is prepared as in Example 1, using 10% NVS PROCION TURQUOISE H-A (ICI) and is utilized in printing as recited above. After removal of the pigmented polymer material, a pale red image is left on printer's stock and on Savin 2000+ paper. There is no background coloring and no image is seen on the reverse side of the paper.

EXAMPLE 11

A liquid developer is prepared as in Example 1, using 10% NVS RHODAMINE B (BASF) and is utilized in printing as recited above. After removal of the pigmented polymer material, a pale red image is left on printer's stock and a vivid red image on Savin 2000+ paper. There is no background coloring and no image is seen on the reverse side of the paper.

CLAIMS

1. A developer for use in electrostatic imaging processes, such developer comprising pigmented polymer toner particles including at least one pigment and at least one sublimable dye.

2. A developer according to claim 1 wherein such developer further comprises an insulating non-polar carrier liquid and said particles are micro-dispersed in said carrier liquid.

3. A liquid developer for use in electrostatic imaging processes, such developer comprising:

an insulating non-polar carrier liquid; and

pigmented polymer toner particles including at least one pigment and at least one dye micro-dispersed in said carrier liquid,

wherein said dye has a low solubility in said carrier liquid at room temperature and a solubility in carrier liquid at fusing temperatures high enough to provide a colored image underlying a final image produced on a substrate after fusing.

4. A liquid developer according to claim 2, wherein said dye is substantially insoluble in the carrier liquid at ambient temperatures.

5. A liquid developer according to claim 3, wherein said dye is substantially insoluble in the carrier liquid at ambient temperatures.

6. A liquid developer according to claim 2 wherein said dye is sufficiently soluble in the carrier liquid at the fusing temperature range such that dye dissolved in said carrier liquid colors regions underlying a final image produced on a substrate after fusing.

7. A liquid developer according to claim 4 or claim 5 wherein said dye is sufficiently soluble in the carrier

liquid at the fusing temperature range such that dye dissolved in said carrier liquid colors regions underlying a final image produced on a substrate after fusing.

8. A liquid developer according to claim 2, 3 or 6 wherein said dye is sufficiently soluble in the carrier liquid at ambient temperatures to provide a colored background for the final image produced on a substrate after fusing.

9. An electrostatic imaging process, comprising the steps of:

forming a latent electrostatic image on a photoconductive surface;

applying to said surface a developer according to any one of the preceding claims, thereby forming a toner image on said surface; and

transferring the resultant toner image to a substrate.

10. An imaging process according to claim 9, which includes a fusing step subsequent to said transferring step.

INTERNATIONAL SEARCH REPORT

International Application No PCT/NL 91/00117

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)[6]

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl. 5 G03G9/12; G03G9/09

II. FIELDS SEARCHED

Minimum Documentation Searched[7]

Classification System	Classification Symbols
Int.Cl. 5	G03G

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched[8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT[9]

Category[10]	Citation of Document,[11] with indication, where appropriate, of the relevant passages[12]	Relevant to Claim No.[13]
Y	EP,A,0 042 139 (PELIKAN AKTIENGESELLSCHAFT) 23 December 1981 see page 9, line 19 - page 10, line 16; claim 1	1,2,4,9, 10
Y	US,A,3 890 240 (DAVID L. HOCHBERG) 17 June 1975 see column 2, line 1 - line 7; claims 1-6	1,2,4,9, 10
Y	PATENT ABSTRACTS OF JAPAN vol. 11, no. 93 (P-559)(2540) 24 March 1987 (MINOLTA CAMERA CO., LTD.) 31 October 1986 & JP,A,61 245 167 see abstract	1,2,4,9, 10
Y	PATENT ABSTRACTS OF JAPAN vol. 6, no. 221 (P-153)(1099) 5 November 1982 (RICOH K.K.) 3 August 1982 & JP,A,57 124 742 see abstract	1,9,10

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* Special categories of cited documents :[10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
19 FEBRUARY 1992	06. 03. 92
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	HINDIAS E.

Form PCT/ISA/210 (second sheet) (January 1985)

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)

Category °	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
A	WO,A,8 803 669 (SRI INTERNATIONAL) 19 May 1988 see page 6, line 25 - page 8, line 10; claim 1 ---	1-10

ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO. NL 9100117 SA 49227

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 19/02/92
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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP-A-0042139	23-12-81	None		
US-A-3890240	17-06-75	DE-A-	2124141	02-12-71
WO-A-8803669	19-05-88	DE-T-	3790582	15-09-88
		EP-A-	0288540	02-11-88
		GB-A-	2204419	09-11-88
		JP-T-	1501258	27-04-89